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Electrochromic transitions in polyaminoarene films electrochemically obtained on transparent electrodes[*]

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The processes of electrosynthesis, electrochemical behaviour and electrochromic properties of polyaminoarenes of different nature and position of substitutents in benzene ring – poly-*o*-(*m*)-aminophenols, poly-*o*-toluidine, poly-*o*-methoxyaniline and polyaniline have been studied in aqueous acid electrolytes. It has been shown that particularities of electrochemical and electrochromic transitions in polyaminoarene films obtained on SnO_2 electrodes are defined by the charge transport parameters depending on the molecular structure of the polymers, type of electrolyte anion and associated with an ion-diffusion phenomena on the polymer–solution interface.

Key words: *polyaminoarene; electrochromic transitions; structure; charge transport*

1. Introduction

Conducting polymers, especially polyaminoarenes such as polyaniline and its derivatives have a potential application as modified electrodes in chemical power sources. During the last years the electrochromic properties of these polymers aroused a great interest [1–3]. It is known that electrochromic displays on the base of organic dyes harmonize with the background and are soft for human eyes, but their erasing-rewriting rate is slow [1]. This rate may be increased by using conducting polyaminoarenes with electroactive chromophore groups [2, 3]. Numerous investigations have been realized for polyaniline films in organic and aqueous electrolytes [1, 3–5] but molecular structure and electrochromic properties of its derivatives, except the poly-*o*-methoxyaniline

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[2, 6], have not been studied in detail. This is particularly true in the case of polyaminophenols, poly-*o*-toluidine and others. In the present paper, we report on the effect of structure and electrolyte on electrochemical behaviour and electrochromic properties of polyaminoarenes of different nature and position of substitutents in benzene ring – poly-*o*-aminophenol (POAP), poly-*m*-aminophenol (PMAP), poly-*o*-toluidine (POTI), poly-*o*-methoxyaniline (POMA) and polyaniline (PANI).

2. Experimental

Preparation of polyaminoarene films was carried out in a three-compartment electrochemical cell by electrolysis of 0.1 M solutions of purified monomers (*o*-toluidine, *o*-methoxyaniline, aniline, *o*- and *m*-aminophenols) in 0.5 M H_2SO_4. The glass, spin-coated with SnO_2 working electrode, Pt-wire counter electrode and Ag/AgCl (in saturated KCl) as a reference were employed. The potentiostat PI-50M was used as a power source. Cyclic voltammetry experiments were carried out on CVA-1 voltamperometric system at potential sweep rate v of 5–200 mV/s. The EPR spectra were recorded *in situ* during the chemical oxidation of 0.1 M aminoarenes by 0.1 M $(NH_4)_2S_2O_8$ in 0.5 M sulfuric acid in quartz cells. The X-band radiospectrometer RE-1306 operating in the high frequency (100 kHz) modulation mode of magnetic field at $T = 293$ K was used. The value of g-factor and unpaired spin concentration were estimated using DPPH as a reference. The UV-Vis absorption spectra were obtained in a quartz electrochemical cell with SnO_2 working electrode using spectrophotometer SF-26 in the 320–1000 nm spectral range. The molecular structure of polymers was studied by IR-spectroscopy by means of the spectrophotometer Specord M-80 (400–4000 cm^{-1} spectral range) for samples pressed in KBr wafers. The content of doping ions was estimated by X-ray microprobe analysis with a Camebax analyzer. Film thickness was measured by micro-interferometer MII-4 or calculated from electrochemical data.

3. Results and disscussion

The formation of electrochromic films of a required thickness on the transparent surfaces may be provided by Langmuir–Blodgett technology [6], or by electrochemical synthesis [3–5]. In the latter case, the regularity of the film thickness may be achieved by the control of the charge passed during electrolysis, and by cyclic voltammetry method [4, 5]. The thickness of the film is determined by sweep cycle number (N) in a certain interval of potentials. In the case of polyaminoarenes, the cycle number and quantity of charge (Q), are connected by the empiric equation proposed by Zotti et al. [5], which for PANI can be written as

$$Q \approx c^2 \left(\frac{N}{\nu}\right)^2 \exp\left[\left(\frac{2\alpha nF}{RT}\right) E_\lambda\right] \quad (1)$$

where Q is the total deposition charge obtained for the fully reduced polymer after N cycles, c – monomer concentration, ν – sweep rate, α – transfer coefficient, n – number of electrons participating in the redox process, F – Faraday's constant, E_λ is the switching potential.

The electrolysis of aminoarene solutions in acid electrolyte at potential of monomer oxidation is accompanied by the formation of conducting polymer film on the metal or oxide electrodes [1–5]. The oxidation proceeds over the aminogen with the formation of cation-radical particles. Previously it has been found that electrochemical oxidation of *o*- and *m*-aminophenols on Pt and graphite electrodes is an irreversible process and proceeds by both (amino- and hydroxyl-) functional groups [7]. It has been established that on transparent tin oxide electrodes the process of oxidation of isomeric aminophenols, unsubstituted phenol and aniline proceeds in similar conditions. Depending on the mutual position of substitutents in benzene ring of the monomer, the oxidative potential (E_{ox}) and the rate of charge transport (k_s) calculated as in [7] are significantly different. As can be seen from Table 1, the presence of hydroxyl groups in aniline molecule and amino groups in phenol molecule causes the decreasing of oxidation potential in comparison with phenol and aniline, and arising of the heterogeneous constant of charge transport for oxidation of OH groups. The rate of aminophenol oxidation over the NH_2 groups is decreased comparably to aniline monomer. This observation is in a good agreement with the data of EPR spectra, presented in the Table 1. In the process of aminoarene chemical oxidation at $T = 293$ K, an EPR signal appears, increasing in time. The shape of line with *g*-factor 2.003 ±0.001 without hyperfine structure is typical of conducting polyaminoarene polymers [8]. The intensity of the signal, recorded after 60 min from the initiation of the polymerization, is significantly higher for aniline oxidation in comparison with aminophenols. A lower intensity of signal, associated with smaller unpaired spin concentration (N_s), broadening of the peak-to-peak distance (ΔHpp) indicates a slower polymerization rate of aminophenols as compared with aniline.

Table 1. Electrochemical parameters of electrooxidation of aminoarenes ($C = 0.1$ M) in 0.5 M H_2SO_4 and characteristics of EPR spectra ($T = 295$ K) of chemical oxidation of aminoarenes

Monomer	Functional group				Parameters of EPR spectra		
	–OH		$-NH_2$				
	E_{ox}/V	$k_s \cdot 10^5$ /(cm/s)	E_{ox}/V	$k_s \cdot 10^5$ /(cm/s)	*g*-factor	ΔHpp/Oe	N_s/(1/g)
Phenol $(C_6H_5)OH$	1.02	4.8	–	–	–	–	–
m-Aminophenol $(C_6H_5)(mNH_2)OH$	0.90	5.4	0.42	4.3	2.0037	8.5	$9.4 \cdot 10^{17}$

o-Aminophenol $(C_6H_5)(oNH_2)OH$	0.62	8.3	0.37	6.7	2.0045	12.8	$6.1 \cdot 10^{18}$
Aniline $C_6H_5NH_2$	–	–	0.80	27.0	2.0036	3.2	$4.7 \cdot 10^{19}$

For electrochemical preparation of polyaminophenol films on SnO_2 electrodes the potential cycling between $E = -0.2$ and 0.8 V with $\nu = 40$ mV/s was used. Coloured polymer films were obtained only after 50 (PMAP) or 60 (POAP) cycles of potential sweeping. The IR-spectroscopy of film material (pressed in KBr pellets) confirmed that in this potential region only the amino group of *m*-aminophenol undergoes anode oxidation while the hydroxyl group remains unchanged. The absorption bands of *para*-substituted aromatic ring (3080, 1520, 760 cm^{-1}), amino group (3350, 1574 cm^{-1}) and OH group at 3600, 1410, 1200 cm^{-1} were found. In the case of *o*-aminophenol the close values of oxidative potentials causes subsequent oxidation by two functional groups, which leads to heterocycle formation [7, 9]. This is confirmed by absorption bands at 1270–1200 cm^{-1} (ether oxygen) and 3400–3200 cm^{-1} (bound hydroxyl). The molecular structure of polyaminophenols in comparison with polyaniline is presented in Fig. 1.

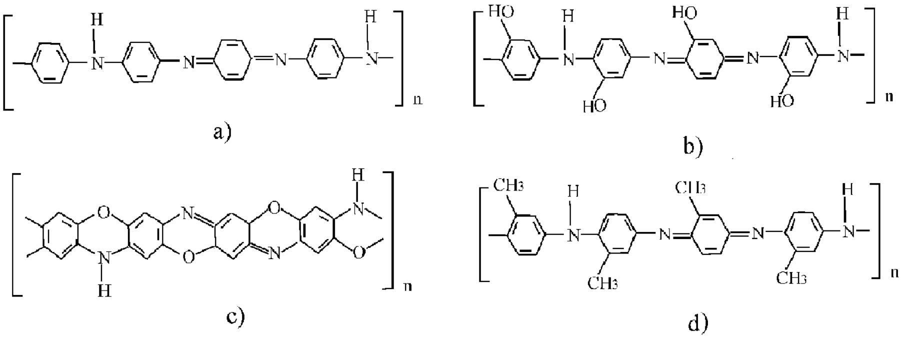

Fig. 1. Molecular structure of polyaminoarenes: a) polyaniline, b) poly-*m*-aminophenol, c) poly-*o*-aminophenol and d) poly-*o*-toluidine

The study of POMA, POTI and PANI films formation on the SnO_2 surface showed that polymerization takes place at significant lower anode potentials ($E = 0.52$–0.70 V) in comparison to monomer oxidation ($E = 0.82$–0.96 V), thus the primary formed layer is the catalyst of the process (Fig. 2a, b).

The polymer formation proceeds by the autocatalytic mechanism according to the known scheme for the reaction of electrochemical coupling of aromatic amines and includes the steps of monomer oxidation over amino group with cation-radical formation and coupling of cation-radicals accompanied by deprotonation [3, 5]. The compact, uniform films of POMA and POTI on the SnO_2 electrodes were obtained after 15–30 cycles of potential sweeping between $E = 0$ and $E = 1.0$ V. The molecular structure of POMA and POTI (Fig. 1d) films obtained in such conditions is similar to PANI and PMAP [3, 6].

In the process of potential cycling in acid aqueous electrolytes between *E* = –0.3 V and *E* = 1.2 V, the reversible multicolour transitions in polyaminoarene films are observed. In the case of POAP the rose-red-brown colouration is observed in the interval of potentials *E* of –0.1–0.4 V. In the case of PMAP the switching potential *E* (yellow -green-brown) lies in a more negative range – from –0.25 V to 0.05 V. For the POTI and POMA films on SnO_2 the colourless-yellow-green-blue-violet transition is observed in the potential interval of –0.3–1.2 V, whereas for PANI film similar colour variations are observed in the range of –0.2–0.8 V [3]. The switching potential of observed electrochromic transitions corresponds to potentials of redox maximums on CVA curves (Fig. 2c, d) which confirm the running of oxidation-reducing reactions in a conjugated polymer chain.

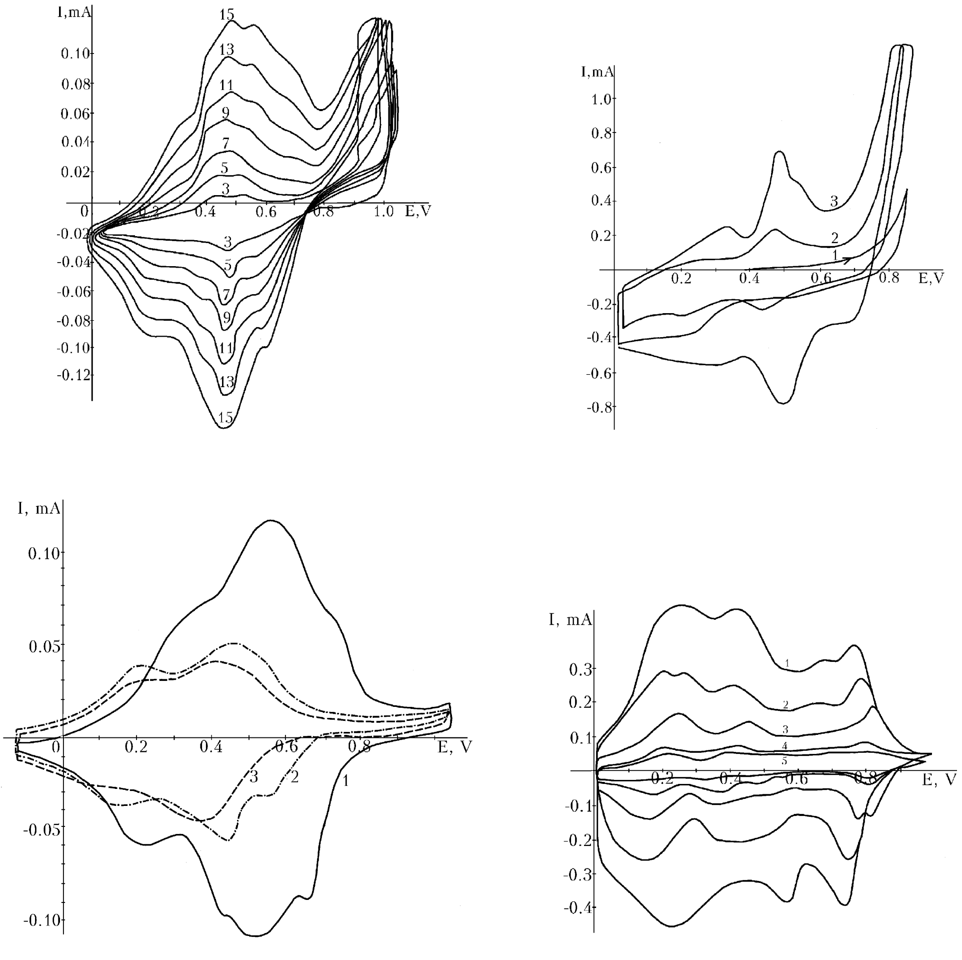

Fig. 2. Cyclic voltammograms obtained in the process of electrodeposition on the SnO_2 electrode: a) poly-*o*-toluidine from 0.1 M *o*-toluidine solution in 0.5 M H_2SO_4; b) poly-*o*-methoxyaniline from 0.1 M *o*-methoxyaniline solution in 0.5 M H_2SO_4, sweep rate 20 mV/s, the numbers refer to the sequence of cycles; c) cyclic voltammograms for poly-*o*-toluidine film in aqueous electrolytes: 0.5 M H_2SO_4 (1); 1 M HCl (2) and 1 M TSA (3), sweep rate 20 mV/s; d) cyclic voltammograms for poly-*o*-methoxyaniline film in 1 M TSA solution at sweep rate 80 (1), 40 (2), 20 (3), 10 (4) and 5 (5) mV/s. The polymer films obtained after 15 cycles of potential sweeping

The influence of anions on polymer redox properties one can see from the CVA curves recorded in acid electrolytes (Fig. 2c, d). In all electrolytes studied (HCl, H_2SO_4, HNO_3, toluenesulfonic acid (TSA)) on the CVA of POTI and POMA films two or three reversible redox peaks are observed. The first peak (E = 0.18–0.25 V) corresponds to the oxidation of fully reduced leucoemeraldine form of polyaminoarene to emeraldine (semiquinone cation-radical) form. The second peak (E = 0.45–0.60 V) is caused by fast oxidation (ΔE < 30 mV) of emeraldine to fully oxidized pernigraniline (dication), where all nitrogen atoms are in the quinone-diimine form [3]. The appearance of small intermediate maxima on the CVA curves may be related to reactions of oligomers or film degradation with formation of a soluble product [10]. Similar to polyaniline, the highest electrochemical activity of POMA and POTI films (estimated as peak current on CVA) has been observed in the sulfuric acid solution. At the same time, a shift of redox potentials to positive values has been observed. It was suggested [10] that anions (especially SO_4^{2-}) strongly interact with radical-cations of polyaminoarenes, promote the localization of charge and facilitate the polymer degradation, since the localized charge is more prone to the nucleophilic attack of water molecules. The highest peak currents are achieved in conditions, in which the process of polymer degradation is difficult. However, those peak currents observed in different electrolytes are also associated with the diffusion of ions on polymer–solution interface [2, 4]. The high peak currents of polyaminoarene films in sulfuric acid may be explained by higher ion mobility of SO_4^{2-} anions in comparison with Cl^- and large TSA anions [11] and strong hydrophilic properties of SO_4^{2-}, determining the kinetics of the electron transfer reaction [4].

The rate of colour transitions is controlled by the electron transport rate in polymer layer immobilized at the electrode surface. This rate may be characterized by the heterogeneous constant of charge transport (k_s) or by the effective coefficient of diffusion (D_{ef}) for charge transport across the film [12]. The study of electrochemical behaviour of polyaminoarene films in acid electrolytes demonstrated that in the case of polyaminophenols, the charge transport is diffusion-limited and a linear dependence of peak current on the square root of the sweep rate ($i_p \sim v^{1/2}$) is observed. This feature permits to calculate the effective diffusion coefficient D_{ef} using model of semi-infinite diffusion [13]. The following equations follow from the model:

$$i_p = 2.69 \cdot 10^5 n^{3/2} S D_{ef}^{1/2} v^{1/2} C^* \tag{2}$$

$$C^* = \frac{Q}{nFSd} \tag{3}$$

where n is the number of electrons participating in the redox process, S – the area of the film (cm^2), C^* – concentration of active centres in the film ($\mathrm{mol/cm}^3$), Q – total charge, calculated by the integration of anode or cathode cyclic voltammetric currents at slow sweep rate, d is a film thickness, F – Faraday's constant.

The calculated values of the effective diffusion coefficients (D_{ef}) for polyaminophenols films in acid electrolytes (Table 2) show that the parameters of charge transport correlate with the absolute mobility of doping anions [11]. The strong difference in the values of the diffusion coefficient found for polyaminophenols and PANI films suggests, however, that the main factor determining the rate of charge transport across the film is the molecular structure and segment mobility of polymer chains. The presence of the electron-donor substitutents in the benzene rings causes, as a rule, some loss of conductivity and electron-transport rate [3]. For the rigid ladder polymer structure of POAP the values of D_{ef} are lower by 2–4 orders compared to PANI, indicating a low rate of charge transport in poly-*o*-aminophenol film.

Table 2. Absolute mobilities of anions (u_c) and effective diffusion coefficients (D_{ef}) of polyaminoarene films in acid solutions

Polyaminoarene film, area and thickness	Electrolyte	u_c, $\mathrm{m^2/Vs}$	$D_{ef} \cdot 10^{10}$, $\mathrm{cm^2/s}$
Poly-*o*-aminophenol, $S = 3.4\ \mathrm{cm}^2$, $d = 0.25$ μm	CH_3COOH (1 M)	3.7	0.0 8± 0.02
	HCl (1 M)	6.8	0.15 ± 0.02
	H_2SO_4 (0.5 M)	7.1	0.23 ± 0.04
Poly-*m*-aminophenol, $S = 4.0\ \mathrm{cm}^2$, $d = 0.28$ μm	HCl (1 M)	6.8	1.17 ±0.07
	H_2SO_4 (0.5 M)	7.1	1.56 ±0.07
Polyaniline, $S = 4.0\ \mathrm{cm}^2$, $d = 0.28$ μm	CH_3COOH (1 M)	3.7	40.2 ± 0.5
	$HClO_4$ (1 M)	6.7	73.7 ± 0.5
	H_2SO_4 (0.5 M)	7.1	90.2 ± 0.5

The best charge transport characteristics were obtained for POMA and POTI thin films. From CVA study in aqueous electrolytes it has been found that electrodeposited polymer layers at $N \leq 15$ demonstrate the electrochemical behaviour attributed to oxidation-reduction of electroactive species strongly adsorbed or immobilized on the electrode surfaces.

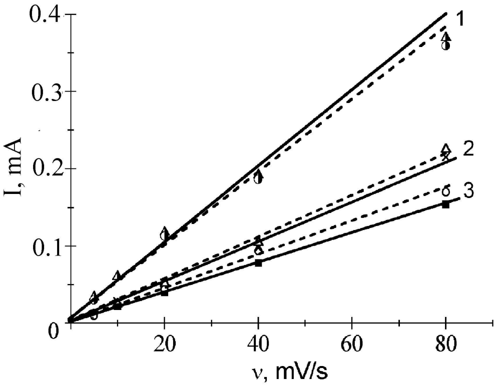

Fig. 3. Peak current dependence on potential sweep rate of poly-*o*-toluidine film in aqueous electrolytes: 0.5 M H_2SO_4 (1), 1 M TSA (2) and 1 M HCl (3); solid line indicates the anode peak and dashed line indicates the cathode peak

The evidences for this behaviour are the high reversibility of redox processes in the films (ΔE is in the range of 30 mV, $I_a/I_\kappa \approx 1$, peak potentials slightly depended on sweep rate) and the linear dependence of anode and cathode peak current (I_a, I_κ) from potential sweep rate ν as shown in Fig. 3.

The doping current i of this polymer layer may be described by the equation [14]

$$i = \frac{n^2F^2A\nu\Gamma_i \exp\theta}{RT(E+\exp\theta)^2}, \qquad \theta = \frac{nF(E-E_0)}{RT} \tag{4}$$

where n is the number of electrons, A – area of the electrode surface, Γ_i – surface concentration of electroactive substances, the sum of concentration of oxidized and reduced form (Γ_{ox} + R_{ed}), E, E_0 – electrode potential and standard electrode potential, F– Faraday's constant. The surface concentration of electroactive substances for POTI film, estimated from Eq. (4) based on i and E parameters of the second CVA maximum in the sulfuric acid solution at ν = 20 mV/cm is nearly 10^{-9} mol/cm^2.

It has been found that in electron spectra of polyaminoarene films changes in positions of absorption maxima and optical densities occur under the potential applied. These changes are accompanied by reversible colour transitions in the films. As is shown in Fig. 4, the shapes of electron spectra of polyaminoarene in sulfuric acid solution depend on the electrode potential and usually are related to the polyaminoarene structure and the nature of functional groups.

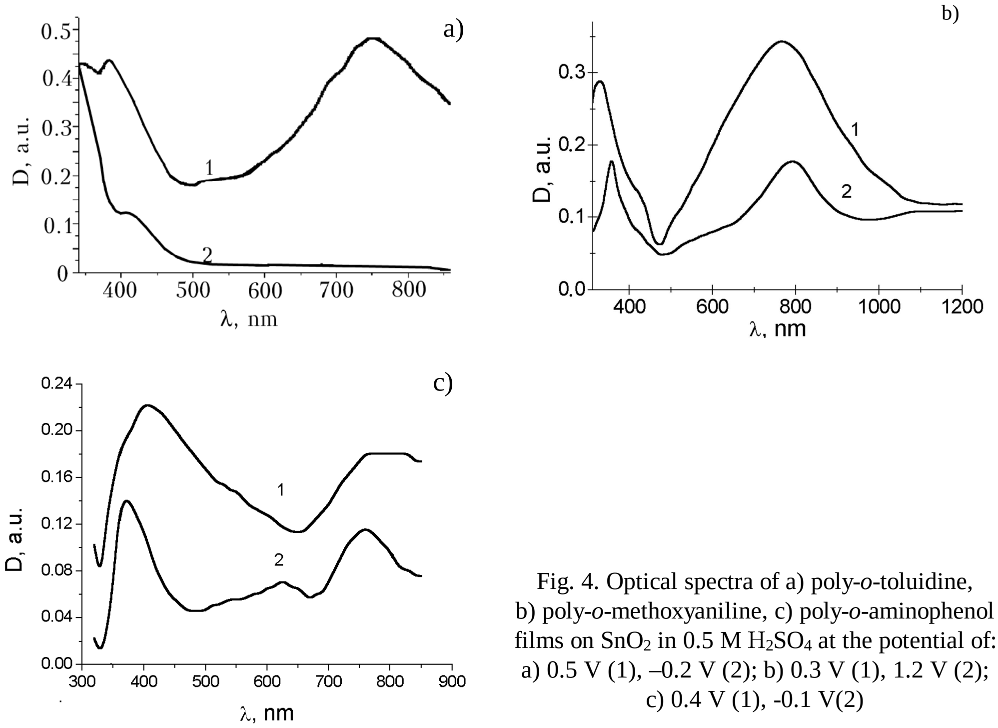

Fig. 4. Optical spectra of a) poly-*o*-toluidine, b) poly-*o*-methoxyaniline, c) poly-*o*-aminophenol films on SnO_2 in 0.5 M H_2SO_4 at the potential of: a) 0.5 V (1), –0.2 V (2); b) 0.3 V (1), 1.2 V (2); c) 0.4 V (1), -0.1 V(2)

Reduction of polymer layers at *E* from –0.2 V to –0.3 V leads to a colourless form of polyaminoarenes with the absorption band at 340–420 nm ($\pi \rightarrow \pi^*$ transition), which is illustrated by curve 2 in Fig. 4a. This band corresponds to leucoemeraldine benzene –amine polymer, which has an unconjugated backbone [3]. The anode polarization of SnO_2 electrode to 0.3–0.6 V causes the appearance of the green colour of PANI, POMA and POTI films, and of rose-red colours of POAP. As is shown in Fig. 4a, b, these transitions for POMA and POTI films similar to PANI [3] are accompanied by arising wide absorption maxima in the visible region of the spectra (700–850 nm). In the case of POAP under anode polarization from –0.1 V to 0.4 V, the intensity of absorption bands in the interval of 600–700 nm increases (Fig. 4c) as a result of polymer oxidation and doping by sulfate anions [9]. A small red shift in the positions of these bands is also observed.

For polymers with linear polymer chain structure, such as POTI, POMA and PANI, the existence of absorption at 340–400 nm and 700–800 nm may be assigned to polaron or bipolaron bands [15]. The existence of a delocalized polaron band is attributed to semi-oxidized states of polyaminoarenes – emeraldine form [3, 10]. The polaron transition is dominant at a lower polarizing potential, while the bipolaron transition is dominant at a higher potential. In the potential interval $E > 0.6$–0.8 V, the blue (PANI, POTI), violet (POMA) and brown (POAP) colours of the films appear, which may be connected with the increase of pernigraniline content in the polyaminoarene. At a still higher potential ($E \geq 1.2$ V), the colour changes become irreversible. The decrease of the optical density for POMA film, taken as an example, (curve 2 in Fig. 4b) takes place as a result of the electrochemical destruction. For all polyaminoarenes studied, the loss of doping level and decrease of the electrical conductivity of the films are observed. According to X-ray microprobe analysis, it has been determined that in the colourless form of polyaniline the contents of doping ions (e.g., sulfate) are close to 0%; in green form – to 6.2 at. %; blue – 3.3 at.% of S.

The features of electrochromic transitions in polyaminoarene films are connected with molecular structure of polymer chains. The incorporation of electron-donating substituents into a conjugated chain leads to the decrease of the polymer oxidation potential by increasing the energy of valence band electrons [15]. On the other hand, the existence of electron-donating substituents in polymer chain ($–OCH_3$, $–CH_3$) leads to the widening of potential range of colour transitions in POMA and POTI films in comparison to PANI [3]. Introduction of the hydroxyl substituent into aminoarene molecule leads to a decrease of the electron transport rate for oxidation of aminophenols and to the formation of rigid heterocycle structure of POAP. The structure obtained, as well as electrochemical and spectroscopic data permit to conclude that electrochromic transitions in conjugated polyaminoarenes are caused by chemical and structural factors. The colour variations depend on the doping level of polyaminoarene connected with oxidation-reduction of aminobenzene or iminoquinoid functional groups. The rate of electrochemical and electrochromic transformations is defined by charge transport in the polymer film associated with diffusion of anions on the polymer–solution interface.

References

[1] YANO J., Electrochem. Soc., 144, (1997), 477.
[2] GONÇALVES D., MATVIENKO B., BULHOES L.O.S., Synth. Metals, 83 (1996), 147.
[3] FOOT P.J.S., SIMON R., J. Phys. D: Appl. Phys., 22 (1989), 1598.
[4] CHOI S.-J., PARK S.-M., J. Electrochem. Soc., 149, (2002), E26.
[5] ZOTTI G., CATTARINN S., COMISSO N., J. Electroanal. Chem., 235 (1987), 259.
[6] GONÇALVES D., BULHOES L.O.S., Thin Solid Films, 243 (1994), 544.
[7] PLUSNINA T.A., AKSIMENTYEVA E.I., KOVALCHUK E.P., Elektrokhimiya, 30 (1994), 825.
[8] AKSIMENTYEVA O.I., ARTYM V.T., MELNIK O.I., PLUSNINA T.A., Acta Phys. Pol. A, 85 (1994), 237.
[9] GONÇALVES D., FARIA R.C., YONASHIRO M., BULHOES L.O.S., J. Electroanal. Chem., 487 (2000), 90.
[10] PALYS B., KUDELSKI A., STANKIEW A., JACKOWSKA K., Synth. Metals, 108 (2000), 111.
[11] DOBOSH D., *Electrochemical Constants*, Mir, Moscow, 1980.
[12] NYASULU F.W.M., MOTTOLA H.A., J. Electroanal. Chem., 239 (1988), 175.
[13] MAKSIMOV YU.M., KHALDUN M., PODLOVCHENKO B.I., Elektrokhimiya, 27 (1991), 739.
[14] LAVTRON E., *Electroanalytical Chemistry*, A. J. Bard (Ed.), Marcel Dekker, New York, 12 (1979), 53.
[15] SANKARAN B., REYNOLDS J.R., Macromolecules, 30 (1997), 2582.

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